SEVENTH QUARTERLY REPORT

21 February through 20 May 1966

Gaseous Electrolytes for Batteries and Fuel Cells

by

S. Naiditch, Principal Investigator

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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TABLE OF CONTENTS

1.0 ABSTRACT

Stable metal amalgam/insoluble salt cells with KCl-NH_3 electrolyte were prepared and run this quarter. Concentrations of the amalgams were established by weights of the components.

Cell emfs were measured at temperatures to $85^{\circ}C$ and were stable to 0.1% over the entire range. Pb(Hg)/$PbCl_2$, Zn(Hg)/Zn Cl_2, Cd(Hg)/$CdCl_2$, and Tl(Hg)/$TlCl_2$ electrodes of 2.35, 3.89, 3.78 and 2.81 mole percent metal respectively were used. From the emf data, we find that Zn and Cd make stable well-behaved electrodes, while phase transitions in the Pb make it less satisfactory. The Tl did not amalgamate well. Comparison of emfs of Pb(Hg)/$PbCl_2$ amalgam concentration with 1.43, 1.30, 1.24 and 1.64 mole percent lead showed a marked difference in behavior between the one and two phase amalgam electrodes.

An analysis of the state of electrolytes in liquid non-aqueous solvents has been carried out jointly on this and Office of Saline Water Contract 14-01-0001-424. In future reports, this analysis will be extended into the dense gaseous phase.

2.0 CELLS USING AMALGAM-INSOLUBLE SALT ELECTRODES

2.1 PREPARATION AND FILLING

Three materials were used to prepare each of the electrodes, mercury, metal and insoluble salt. The mercury was triple distilled reagent grade and was used without further purification. The lead, zinc, cadmium, and thallium were reagent grade and had less than 0.01% metallic impurities. Surface oxide was visible on both the lead and thallium. The lead and zinc were in granular form and the cadmium and thallium were turnings.

The salts, anhydrous reagent grade, were ground, dried for 48 hours at $125^{O}C$, and cooled and stored under vacuum in a desiccator until just before use.

The cells to be filled were first cleaned with a glass cleaner, rinsed with distilled water, and oven dried. Weighed amounts of mercury were then introduced through filling tubes into each electrode compartment. Next, under dry nitrogen, a weighed amount (about 0.1 gm.) of metal and a small amount of insoluble salt were introduced into each electrode compartment. The insoluble salts were not weighed because they are very hygroscopic. These salts were introduced at the last possible moment before evacuation in order to minimize contamination. After filling and sealing the filling tubes, the cells were attached to the vacuum preparation system and evacuated. At this point it was found that cell 61 had a small crack, and was removed from the system. Cell 61 will be repaired and reused

TABLE 1

ELECTRODE CONSTITUENTS OF THE INSOLUBLE SALT-AMALGAM ELECTRODES

CELL	KCl WT.GM	ELECTRODE											
		A			B			C			D		
		METAL	METAL WT.	Hg WT.	METAL	METAL WT.	Hg WT.	METAL	METAL WT.	Hg WT.	METAL	METAL WT.	Hg WT.
71	1.0490	Pb	0.1114	7.4369	Pb	0.1108	8.17	Pb	0.1074	8.3740	Pb	0.1164	6.7774
61	1.0234	Zn	0.1064	5.1766	Pb	0.1251	10.4687	Pb	0.1334	9.3241	Zn	0.1041	4.1380
60	1.1235	Tl	0.1132	6.2566	Pb	0.1107	7.3015	Pb	0.1159	5.8453	Tl	0.1193	7.2156
68	1.0841	Cd	0.1137	6.3337	Pb	0.1212	6.9631	Pb	0.1538	6.2708	Cd	0.1050	6.3953
70	1.0656	Pb	0.1446	5.8078	Zn	0.1145	8.6881	Tl	0.1020	6.7836	Cd	0.1498	6.8028
69	1.0301	Pb	0.1215	8.3533	Zn	0.1596	8.0604	Tl	0.1230	12.9182	Cd	0.1134	7.0534

In order to minimize volatile contaminants, the cells were evacuated to 2×10^{-5} torr for four days at room temperature, at which point heating with hot water no longer caused an increase in pressure. Each cell was then subjected to ultrasonic agitation for 2 to 4 hours, under vacuum, at 50 to 100°C. The agitation, which was intended to speed amalgamation, was not completely successful. At the time of filling, all the electrodes looked nonuniform, with those containing thallium showing no visible signs of amalgamating. The agitation did, however, distribute the salt in a uniform layer over the electrodes.

After four days on the vacuum system, two cells were filled with a solution of KCl in NH_3. The KCl had been weighed and placed in a trap above the cells before evacuation. It was planned to wash the KCl, which is slightly soluble in ammonia at -40°C, quantitatively into the cell by re-cycling ammonia from the cell to the KCl trap and back. Because of poor ammonia flow in the capillary tube, the rate of KCl transfer was slow, and only about 25% of the KCl was transferred.

After two cells were filled, the remaining three were held under vacuum for two more days. After this additional pumping, the ammonia flowed more freely down the capillary interconnecting tube than earlier. Part of the difficulty was due to the fact that the cells cannot be baked under vacuum because of the volatility of the electrode materials. Additional pumping removed some of the materials that are normally removed by vacuum bakeout. In the future we plan to place KCl in the cell and condense the ammonia directly from the vapor state into the cell instead

of running it down the capillary as a liquid.

After filling and storage in the refrigerator at $0^{\circ}C$, cell 68 broke for unknown reasons and cell 69 cracked during preparation for mounting.

TABLE II

MOLE % METAL IN THE METAL AMALGAMS

CELL	ELECTRODE			
	A	B	C	D
71	1.43% Pb	1.30% Pb	1.24% Pb	1.64% Pb
60	3.36% Tl	1.47% Pb	1.88% Pb	3.81% Tl
70	2.35% Pb	3.39% Zn	2.81% Tl	3.78% Cd

2.2 CELL 70

After storage at $0^{\circ}C$ for three days, Cell 70 was mounted in the pressure vessel in the usual manner. This procedure consists of first covering the exposed leads with Teflon sleeving, then attaching the bomb leads, and last, wrapping Teflon sheet around the entire cell assembly. The cell was then inserted in the bomb and allowed to stand under excess external pressure for three days at $20^{\circ}C$ to permit completion of the amalgamation process. The cell temperature was then increased at the rate of $50^{\circ}C$/day to $150^{\circ}C$. It was planned to hold the cell at $150^{\circ}C$ for 24-48 hours to insure amalgam uniformity, then return to lower temperatures for detailed studies. We hoped in this manner to prevent equilibrium problems such as occurred earlier with cell 57[*].

The cell was successfully heated to $150^{\circ}C$; however, after about 1 hour at that temperature, a small crack developed and the ammonia was lost. As a result of the crack the bomb pressure will be increased in future runs.

In its three days of testing, cell 70 provided a great deal of useful information. The emfs were stable to 0.05% and internally consistent to better than 1% at $85^{\circ}C$. This is an improvement of many orders of magnitude over previous cells using amalgam-insoluble salt electrodes. Not only were the three electrodes which we had used earlier, $Zn(Hg)/ZnCl_2$, $Tl(Hg)/TlCl_2$, and $Cd(Hg)/CdCl_2$, stable for the first time, but so also was the $Pb(Hg)/PbCl_2$ electrode. This was the first measurement made with this electrode.

[*]Fifth Quarterly Report, p. 16

-5-

TABLE III

MEASURED EMFS FOR CELL 70

TIME HOURS	TEMP °C	ELECTRODE					
		Cd - Pb 1 DA	Cd - Tl 2 DC	Cd - Zn 3 DB	Pb - Zn 4 AB	Pb - Tl 5 AC	Zn - Tl 6 BC
0	20	-0.40283	-0.328	0.41766	0.82036	+0.0764	-0.743
24	45	-0.33859	-0.289	0.41298	0.75134	+0.05100	-0.7020
30	76	-0.34672	-0.4056	0.3979	0.7433	-0.05998	-0.8031
46	82	-0.3784	-0.2497	0.39651	0.7750	+0.1275	-0.6488

Current drawn on cell in attempted impedance measurements

| 54 | 81 | -0.32632 | -0.2216 | 0.40552 | 0.73154 | +0.1079 | -0.6269 |

In addition to the attainment of stability, several correlations can be made. Both the Cd (D) and Zn (B) electrodes appear to be well behaved. The data for Cd vs Zn are summarized below.

Time, hours	0	24	30	46
t, °C	20	45	76	82
E, mv	418	413	398	397
ΔE, mv		-5	-15	-1
$\frac{\Delta E}{\Delta T}$, $\frac{mv}{°K}$		-0.2	-0.5	-0.2

It is seen that the emf changes in going from 20 to 76°C are small. Furthermore, after 16 hours at 76-82°C, the emf did not change appreciably (0.3%). The emf did change after current was passed through the Cd electrode (D). We shall use these two electrodes as reference electrodes in examining the behavior of the Pb and Tl electrodes.

As seen from Figure 1, there will be a transition in behavior of the 2.35 mole % Pb electrode at 36°C. If one compares the data at 20 and 45°C above and below this transition temperature one sees that there are large emf changes in the Pb electrodes, whereas in the next temperature interval, the effects are much smaller. Hence we attribute the large change in emfs of the Pb electrode in going from 20 to 45°C to the phase transition.

Time, hours	0		24		30		46
t, °C	20		45		76		82
Pb-Zn (AB)							
E, mv	820		751		743		775
ΔE, mv		-69		-8		+32	
Pb-Cd (AD)							
E, mv	403		339		347		378
ΔE, mv		-64		+8		+31	

At still higher temperatures (80°C), when held for 16 hours, there is an apparent equilibration effect. We have not yet accounted for this effect.

In the case of the Tl electrode, we observed visually, when preparing the cells, that there appeared to be little or no amalgamation. The data indicate that amalgamation was occurring during the heating cycle, so that the Tl electrodes were never homogeneous. This can be seen in the data for the TlZn (CB) and TlCd (CD) cells. For example, on heating for 16 hours at 80°C, the emfs in these two cells decreased by 154 and 156 mv respectively.
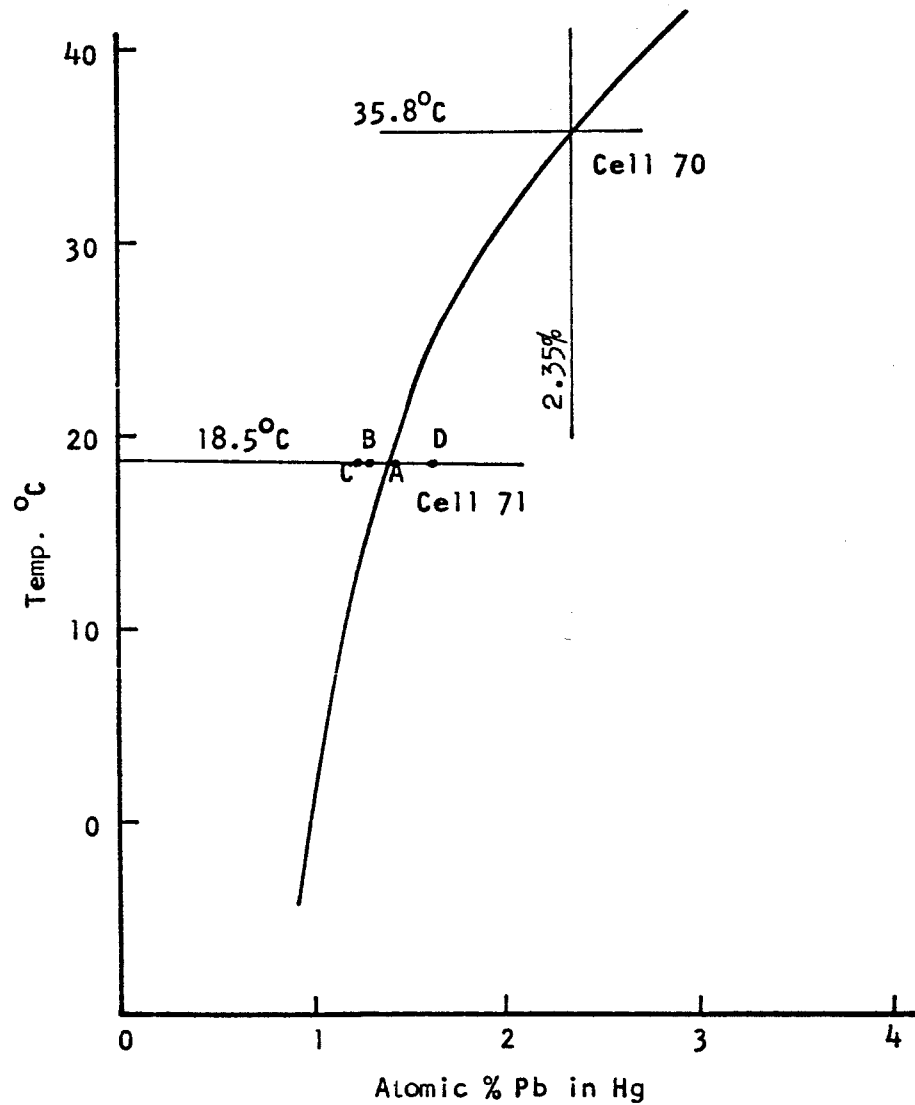
Figure 1. Phase Diagram for the Mercury-Lead System

2.3 CELL 71

In this cell, four lead amalgam-lead chloride electrodes were used. The emfs at 18.5°C were stable to 0.1% and consistent to 5%. When these emfs are compared with ones calculated assuming unit activity coefficients* (Table 4), it is seen that the three electrode pairs involving the most concentrated amalgam, D, show a uniformly large difference. Examination of the phase diagram (Figure 1) shows that amalgam D is in the solid phase. In Figure 1, the curve should pass to the right of amalgam A. (The sensitivity or accuracy of the present method may be higher than that used to determine the phase diagram).

When the cell was heated to 50°C, it failed after a few hours due to a flaw in the glass.

TABLE IV

Measured and Calculated Emfs for Cell 71 at 18.5°C Using Lead Amalgam-Lead Chloride Electrodes

Electrode	Measured	Calculated	Difference
DA	+0.947 mv	-1.73 mv	-2.68 mv
DC	-1.415	-3.51	-2.09
DB	-0.766	-2.91	-2.14
AB	-1.665	-1.19	0.47
AC	-2.393	-1.77	0.62
BC	-0.754	-0.602	0.15

*The emfs were calculated from: $E = \frac{RT}{NF} \ln(c_1/c_2)$

3.0 THE NATURE OF DENSE GASEOUS ELECTROLYTIC SOLUTIONS

Until recently, we were unable to make satisfactory, detailed predictions of
the differences in electrochemical behavior between the liquid and dense
gaseous electrolytic states. In the meantime, on another program (OSW
Contract 14-01-0001-424) we produced data needed for our analyses. Using
these data, we have been making an analysis, jointly on both programs to
avoid duplication, of the nature of liquid electrolytes. Now we are starting
to extend this analysis to predict the differences in the electrochemical
behavior of liquid and dense gaseous electrolytes. The first section of
these analyses, that on liquid electrolytes, is given in the following.

In the OSW program, we developed a technique for measuring directly the energy
of attachment of solvent molecules to positive ions in vacuum. We have used
ammonia since the rate of reaction of alkali metals with ammonia can be kept
at a low level during the time in which we run the experiments. As an
example, we have successfully studied mixtures of Na (liquid and gas) and
NH_3 (gas) at $350^{\circ}C$.

In the analysis that follows, we first convert the experimentally measured
energy of attachment of NH_3 to Cs^+ into the corresponding process in the
liquid state. Then we apply this result to the ionization of CsCl in NH_3.

3.1 BACKGROUND

The approach we are using follows that in Fowler and Guggenheim[*] in accounting for the properties of electrolytic solutions. First they calculate the ionization constant of NaCl in the perfect gas state. They find that for

$$NaCl = Na^+ + Cl^-,$$

$K_G = 10^{-89}$. They then introduce into their equations a uniform dielectric constant equal to that of H_2O, obtaining

$$K_D = 7$$

Thus, the introduction of one property of water, its large dielectric constant, accounts for much of the ionization of NaCl in H_2O. They ascribe the difference between K_D and complete dissociation to solvation but do not calculate the increase in the ionization constant due to it. In the following, we shall determine the magnitudes of both the effects of dielectric constant and solvation on ionization constants. In a later report, we shall extend these analyses to the dense gaseous electrolytic state.

[*]Fowler and Guggenheim; Statistical Thermodynamics, Oxford.

3.2 CsCl in Liquid Ammonia at $-33^{\circ}C$

We shall refer all data in this section to the boiling point of liquid ammonia, $-33^{\circ}C$ ($240^{\circ}K$), since this is the common working temperature for ammonia studies.

In the OSW program, we have measured the energy of attachment ΔE_A of one NH_3 by Cs^+ in the low pressure gas phase,

$$Cs^+ + NH_3 = CsNH_3^+; \qquad \Delta E_A = -6.6 \pm 0.9 \text{ kcal/mole} \qquad (1)G$$
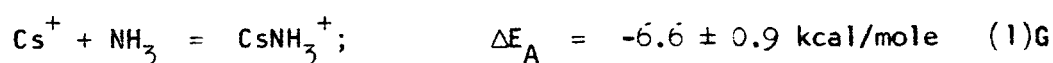
where the symbols after equation numbers, G, H, D, are used to indicate the (fictitious) media to which the equations refer. G refers to low pressure gaseous media, H to media with the same hydrogen bonding as in liquid ammonia, D to media with a uniform dielectric constant equal to that of liquid ammonia, and HD to media with both the hydrogen bonding and dielectric constant of liquid ammonia.

We need the energy of attachment ΔE_H for the corresponding process in the liquid state. In carrying out this analysis, we shall consider a fictitious liquid or fluid in which the hydrogen bonding is identical to that in liquid ammonia. This is equivalent to assuming that the principal difference between the process in the low pressure gaseous state, and that in the liquid state, can be attributed to the presence of hydrogen bonds, and that the effect of dielectric constant on energy of attachment can be neglected. We therefore write the process in the liquid state as follows:

$$Cs^+ + NH_3 \cdot Am + CsNH_3^+ \cdot Am \qquad (2)H$$

where the symbol Am indicates that the species is in solution in the hydrogen-bonding medium, NH_3. We shall denote the change in energy for this process by ΔE_H.

3.2.1 Hydrogen Bond Energy in Liquid Ammonia

We assume that when an ammonia molecule coordinates to a cesium ion in ammonia, one half of its hydrogen bonds with the neighboring ammonia molecules are unaltered; the other half are replaced by a Cs^+-N coordinate bond, and the van der Waal energy in the neighborhood of the ion is un-affected.
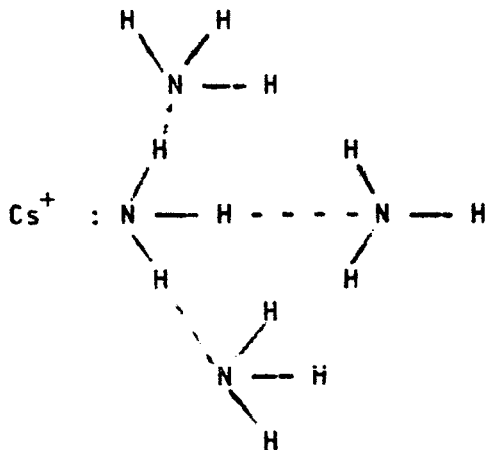
In the solid state, each N is covalently bonded three hydrogens and hydrogen-bonded to three additional hydrogens. The number of hydrogen bonds is less in the liquid state than in the solid state, since the temperature is higher and since the liquid is not rigid. However, for the present analysis, we do not need to know the number of hydrogen bonds but only that half are replaced by a Cs^+.

Pauling[*] has examined the bonding energy in solid ammonia. This energy, which is equal to the heat of sublimation, is assumed to consist of two parts: the van der Waal energy and the hydrogen bond energy. He makes the estimate that the van der Waal energy in the solid is 2.6 kcal/mole, and combines this with the experimental heat of sublimation to obtain the hydrogen bonding energy in the solid.

In order to use this procedure in the liquid, we need an estimate of the van der Waal energy in that state. Since the van der Waal energy is inversely proportional to the sixth power of the interatomic distance, we have taken the ratio of the squares of the molal volumes as providing a rough measure as to how the van der Waal energy changes with temperature. Subtracting this estimated value of the van der Waal energy from the heat of vaporization of the liquid at $-33^\circ C$, we then obtain the total hydrogen bond energy per ammonia at $-33^\circ C$ ($240^\circ K$).

$$E(\text{hydrogen bond}) = \Delta H_V - E(\text{van der Waal})_S \left(\frac{V_S}{V_T}\right)^2$$

$$= 5.567 - 2.6\left(\frac{21.3}{24.99}\right)^2$$

$$= 3.7 \text{ kcal/mole}$$

where the subscript s refers to the solid state.

[*]Pauling, <u>Nature of the Chemical Bond</u>.

3.2.2 Hydrogen Bonding to the Solvated Ion, $CsNH_3^+$ in NH_3

We shall now examine hydrogen bonding to $CsNH_3^+$ in NH_3. This bonding can only take place through the three H's in this ion. We assume that the van der Waal energy is uniform throughout the liquid; i.e., that there are no local changes in van der Waal energy when an ammonia molecule partially leaves the ammonia environment and coordinates to the cesium ion. Hence, we consider only the effects of breaking hydrogen bonds. We shall assume that the number of hydrogen bonds associated with the three hydrogens of a solvated ammonia is not changed by the solvation process, although the polarization of the solvated NH_3 is undoubtedly different than that of the NH_3 in the solvent itself. The hydrogens on the $CsNH_3^+$ ion hydrogen bond with the solvent so that the solvated ammonia molecule retains approximately half of its hydrogen bond energy; i.e., $1/2 \times 3.7$ or 1.8 kcal/mole. Thus, ΔE_H (cf. eq. (2)) is equal to the difference between the energy of attachment and half of the hydrogen bond energy associated with an ammonia molecule in ammonia at $-33°C$. From this, we find that

$$\Delta E_H = \Delta E_A + 1/2 E_{HB}$$

$$= -6.6 + 1.8 = -4.8 \text{ kcal/mole}$$

The hydrogen bond-breaking term introduced here or similar terms will occur in all associated solvents.

3.2.3 Ionization of CsCl

Having determined ΔE_H, we shall now discuss the ionization of CsCl in NH_3. In the following table, ΔH_G is obtained from the literature. ΔH_D is simply $\Delta H_G/D$ where the dielectric constant for NH_3 is $D = 22.4$. ΔH_H has been deduced in the preceding section, and ΔH_{DH} is the sum of ΔH_D and ΔH_H.

TABLE V

$$CsCl = Cs^+ + Cl^- \qquad \Delta H_G = 110 \text{ kcal/mole}^{[1]}$$
$$\Delta S_G = 8.52 \text{ cal/mole/}^{\circ}K^{[2]}$$

$$CsCl = Cs^+ + Cl^- \qquad \Delta H_D = \frac{110}{22.4} = 4.9 \text{ kcal/mole}$$
$$\Delta S_D = 8.52 \text{ cal/mole/}^{\circ}K^{[3]}$$

$$Cs^+ + NH_3 \cdot Am = CsNH_3^+ \cdot Am; \qquad \Delta H_H = -4.8 \text{ kcal/mole}^{[4]}$$
$$\Delta S_H^{[5]}$$

$$CsCl + NH_3 \cdot Am = CsNH_3^+ \cdot Am + Cl^-; \qquad \Delta H_{DH} = 0.1 \pm 0.9 \text{ kcal/mole}^{[6]}$$
$$\Delta S_{DH}^{[7]}$$

[1] Bauer and Porter, p. 6-2 in Blander, Ed., Molten Salt Chemistry, Interscience, 1964.

[2] Calculated from the partition functions assuming no vibrational excitation.

[3] Assuming no effect of dielectric constant.

[4] In the liquid state, $\Delta H_1 = \Delta E_1$ since $\Delta(pV)$ is negligible.
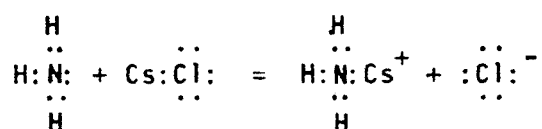
[5] We have not yet evaluated this.

[6] $\Delta H_{DH} = \Delta H_D + \Delta H_H$. The indicated error does not yet include the error in the hydrogen bond error.

[7] $\Delta S_{DH} = 8.52 + \Delta H_H$.

ΔS_G has been calculated from the partition functions assuming no vibrational excitation. In taking $\Delta S_D = \Delta S_G$, it is assumed that the Cs-Cl distances in the molecule (ion pair) in solution is the same as in the gas phase. When the computation of ΔS_H is completed, we will then be able to calculate the ionization constant of CsCl in NH_3.

The approximate equality of ΔH_D and ΔH_H is interesting. It means that the net bonding energies of Cl^- and NH_3 to Cs^+ in NH_3 are about equal. It would appear that the cesium ion in solution is generally sharing one or more electron pairs as follows:

$$
\begin{array}{l}
\quad H \qquad\qquad\qquad\quad H \\
\quad \overset{\cdot\cdot}{} \qquad \overset{\cdot\cdot}{} \qquad\qquad \overset{\cdot\cdot}{} \qquad\quad \overset{\cdot\cdot}{} \\
H\!:\!\overset{\cdot\cdot}{N}\!: + Cs\!:\!\overset{\cdot\cdot}{Cl}\!: \;=\; H\!:\!\overset{\cdot\cdot}{N}\!:Cs^+ + :\!\overset{\cdot\cdot}{Cl}\!:^- \\
\quad \overset{\cdot\cdot}{} \qquad \overset{\cdot\cdot}{} \qquad\qquad \overset{\cdot\cdot}{} \qquad\quad \overset{\cdot\cdot}{} \\
\quad H \qquad\qquad\qquad\quad H
\end{array}
$$

The cesium ion in ammonia thus shares an electron pair on a relatively impartial basis with any of its neighbors. In this sense, the chloride plays the same role as the ammonia in providing the electron pair. Hence, insofar as the innization process is concerned, the environment of the Cs^+ is not changed very much in the ion-paired versus solvated ionic states in solution.

Two items are needed to complete the evaluation of the interpretation under development herein: (1) additional energies of attachment for a second and possibly a third NH_3 to Cs^+; and (2) the remainder of the entropy calculations.

4.0 PRESSURE VESSEL

During the last quarter, the bomb failed due to a small piece of mercury lodging between the heater and a coolant tube. The short caused by this mercury burned a 1/16 in. dia. hole in the tube and melted about 1/2 inch of heater. As a result of the involved repairs, patching the hole, splicing the heater and re-cementing the bottom third of the bomb, two fittings in the coolant lines leak slightly. To avoid spending further time on repairs as we are not currently using the coolant system, we have temporarily capped the coolant lines.

5.0 CONCLUSIONS

We have produced metal amalgam-insoluble salt electrodes in ammonia that are stable to at least 60°C. This progress is based on our studies on sodium amalgam concentration cells.

Both $Zn(Hg)/ZnCl_2$ and $Cd(Hg)/CdCl_2$ electrodes were well behaved and stable. Use of $Pb(Hg)/PbCl_2$ electrodes is complicated by the presence of different phases in the range of concentrations that we used. Because of this, we have not examined the data to see whether the high temperature changes in these electrodes may be due to a slow disproportionation or ammonolysis.

Workers at room temperature have used 1.8 - 56% lead amalgams, since then there coexist two metallic phases, so that the electrode potentials are independent of composition. There are two difficulties in using these for our work: (1) when the temperature is changed, long times may be required for equilibration, and (2) crossing a phase boundary at 140°C will cause problems as we wish to operate at up to 200°C.

Thallium did not amalgamate as readily as did Pb, Cd, Zn, so that the thallium electrodes will be re-examined in the future.

The nature of solutions of electrolytes in liquid ammonia have been examined in detail. We plan to extend these analyses to the dense gaseous state.

6.0 NEXT QUARTER

During the next quarter, more metal amalgam-insoluble salt cells will be filled Two changes are planned in our equipment. First, a new cell filling system is now being designed which will speed the filling and reduce the risk of run loss due to breakage. Continued studies of the electrode properties and electrode-electrolyte interactions will be carried out, using metal amalgam-insoluble salt cells.

Second, plans are now being made to modify the small pressure vessel to allow the running of cells in it. In order to make this practical, its head must be identical with that of the large vessel now used. This will require minor modification of the small vessel and the purchase of several head blanks. These two modifications in our equipment will speed data collecting and make it more responsive to the immediate needs of the program by reducing lead time.

In addition, there are now two amalgam concentration cells in cold storage. Though our principal interest has moved to the metal amalgam-insoluble salt cells, we plan to run them as soon as time permits. These runs will be aimed particularly at getting data in the super-critical region.